

**Mestrado Integrado em Engenharia Química**

***Low density starch-based composite foams***

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“Põe quanto és no mínimo que fazes.”

Ricardo Reis

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## Abstract

Nowadays lightweight materials are trending in the furniture industry, as the reduction of weight is required for economic and transportation reasons. This work investigates the feasibility of developing a new lightweight starch-based composite foam to be used in furniture as a core in a sandwich panel. Furthermore, the foam should be produced with microwave heating, for being an inexpensive and fast technique.

To the main ingredient of the foam, starch, were added water, sodium hydrogen carbonate fibers and chitosan, each with a specific function like blowing agents, fillers and crosslinking agents. Several foams with variable pH and variable content of sodium hydrogen carbonate, fiber, chitosan and water were produced as to evaluate the influence of each compound on the foams mechanical properties. Relevant properties of the produced foams were evaluated including: density, internal bond, moisture content and compressive modulus. Low density starch-based composite foams were produced with densities between 147 kg/m<sup>3</sup> and 380 kg/m<sup>3</sup>.

The best formulation corresponded to the foam with a density of 181 kg/m<sup>3</sup>, an internal bond strength of 0,24 N/mm<sup>2</sup> and a compressive modulus of 0,086 MPa.

**Keywords (theme):** starch, foam, microwave foaming, composites, mechanical properties

## Resumo

Atualmente materiais leves estão a tornar-se numa tendência na indústria do mobiliário. A redução do peso é muito apreciada tanto por razões económicas como para facilitar o transporte.

Este trabalho investiga a possibilidade de desenvolver um material compósito de baixa densidade baseado em espuma de amido para ser usado na indústria de mobiliário como núcleo de um sistema de painel sanduíche. Além disso esta espuma será produzida através de aquecimento por micro-ondas, visto que é uma técnica relativamente barata e rápida.

Ao amido, ingrediente principal da espuma, foram adicionados outros como: água, bicarbonato de sódio, fibras e quitosano, cada um com uma função muito específica tal como agente de expansão, carga e agente reticulante.

Foram produzidas diversas espumas de amido fazendo variar o pH da pasta inicial e variando também a quantidade adicionada de bicarbonato de sódio, fibras, quitosano e água de forma a avaliar a influência de cada um destes compostos nas propriedades mecânicas da espuma. As propriedades mais relevantes das espumas produzidas foram analisadas, incluindo a densidade, a resistência interna, o teor de humidade e ainda o módulo de compressão. Daqui resultaram espumas de baixa densidade com densidades entre 147 kg/m<sup>3</sup> e 380 kg/m<sup>3</sup>.

A melhor formulação encontrada correspondeu à espuma com uma densidade de 181 kg/m<sup>3</sup>, uma resistência interna de 0,24 N/mm<sup>2</sup> e um módulo de compressão de 0,086 MPa.

**Palavras-chave (Tema):** amido, espumas, aquecimento por micro-ondas, compósitos, propriedades mecânicas

## Declaration

I hereby declare, on my word of honor, that this work is original and that all non-original contributions were properly referenced with source identification.



*Maria Inês Monteiro Carvalho*

July of 2018



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## Notation and Glossary

$d$	density	$\text{kg/m}^3$
$l$	length	m
$h$	height	m
$w$	width	m
$f$	frequency	Hz
$P$	power	W
$t$	time	min
$T$	temperature	$^{\circ}\text{C}$
$v$	rotational speed	rpm
$F$	Force	N
$p$	Pressure	MPa
$V$	Volume	$\text{m}^3$
$m$	Mass	kg
$A$	Area	$\text{m}^2$
$IB$	Internal Bond strength	$\text{N/mm}^2$

### *List of Acronyms*

PCL	poly ( $\epsilon$ -caprolactone)
PHEE	poly (hydroxyester ether)
PLA	poly (lactic acid)
PVA	poly (vinyl acetate)
PU	polyurethane
SEM	Scanning Electron Microscopy
WAXS	Wide-angle X-Ray scattering



# 1 Introduction

In recent years lightweight materials are becoming a trending issue in the industry. The reduction of weight is required for many reasons. First of all, for economic reasons: fewer materials are needed and the transportation costs are consequently lower. Also, the increase of mobility of people challenges the industries to develop products which can be easily handled and transported by the final customer. (Monteiro, Martins, Magalhães, & Carvalho, 2018)

Lightweight panels are those with density below  $600 \text{ kg/m}^3$ . Honeycomb panels and panels with foam core are also included.

## 1.1 Work objectives

The aim of this thesis is to develop a new lightweight starch-based composite foam using renewable resources. This foam is going to integrate a sandwich panel like system.

As mentioned in the previous section, lightweight materials must have a density below  $600 \text{ kg/m}^3$ . Therefore, to produce the core of a lightweight panel, it should have less than  $400 \text{ kg/m}^3$ , so that both external surfaces may have a higher density.

One of the objectives is also to produce this foam via microwave heating. This technology will be further explained in the next chapter, though, it was selected mainly because it is a very quick process.

In literature, most of the experiments using microwave heating start from extruded pellets. However, in this work the purpose is to start from a paste.

This work will optimize the formulation of the foam, evaluating the effects of the different raw materials and defining their optimal content in the final formulation resulting in a combination of low density and high internal bond of the foam.

## 1.2 Organization of the thesis

The layout of this work is as follows.

In Chapter 2 are summarized the studies in this field. This chapter is divided in three sections: Starch (Section 2.1), which describes briefly the structure, properties and applications of starch; Starch Foaming Techniques (Section 2.2) and Modification of starch-based foams (Section 2.3).

Chapter 3 introduces the materials and methods used in the development of the project.

The experimental results are discussed in Chapter 4. Firstly, the influence of the pH (Section 4.1) and the content of sodium hydrogen carbonate was studied (Section 4.2).

Next in Section 4.3 it is discussed the content of fiber, of chitosan (Section 4.4) and of water (Section 4.5), followed by section 4.6 where the results of the optimal formulation were presented.

Finally, Chapter 5 summarizes the main conclusions of this work, presents this project's limitations and suggests future works.

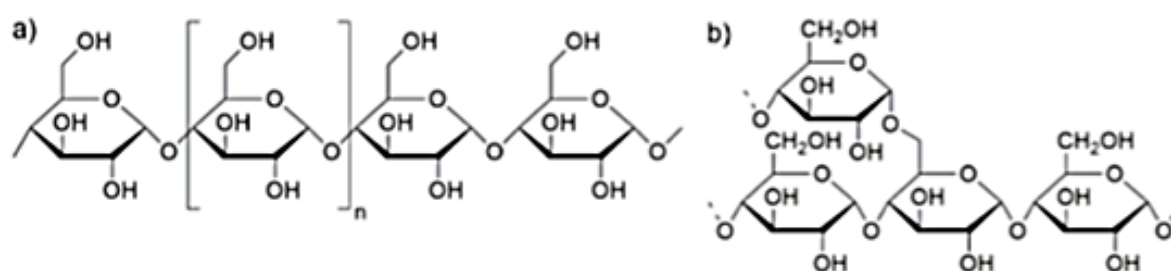
## 2 State of the art

The development of the current materials and products is being led by sustainability, industrial ecology, eco-efficiency and green chemistry. There is a growing concern to develop new bio-based products, independent of fossil fuels. Eco-friendly bio-composites are of considerable importance to material science, providing an answer to both uncertainty of petroleum supply and to environmental threats. (Mohanty, Misra, & Drzal, 2002)

### 2.1 Starch

Starch is one of the most abundant polymers present in nature, as well as a renewable and inexpensive commodity. It is the major form in which carbohydrates are stored in many plants. Starch can be found in cereal grains, such as corn and wheat, tubers (potatoes) and roots. It exists in small granules, which can occur in several shapes and sizes, depending mostly on botanical origin. Common shapes include spheres, polygons, ellipsoids among others. Their sizes can be as high as 100  $\mu\text{m}$ . Potato starch, in particular, has oval and spherical granules with sizes ranging between 15-75  $\mu\text{m}$ .

Starch consists of two macromolecules, amylose and amylopectin (Figure 1). Amylose is the smallest of the two molecules and is a mainly linear polymer, with  $\alpha$ -(1 $\rightarrow$ 4) linked glucose units. Its molecular weight ranges between  $10^4$  to  $10^5$  and can have a degree of polymerization as high as 600. Amylopectin, on the contrary, is a highly branched molecule and the major component of the starch granule. It has an  $\alpha$ -(1 $\rightarrow$ 4) linked glucose joined by  $\alpha$ -(1 $\rightarrow$ 6) branch linkages and has a molecular weight in the order of  $10^6$  to  $10^8$ , resulting in a degree of polymerization up to 50 000 units. (Pérez, Baldwin, & Gallant, 2009)



**Figure 1:** Molecular structure of amylose (a) and amylopectin (b). (Monteiro *et al.*, 2016)

Some starches, from potato mostly but also from other roots, have substituted phosphate esters at C-6 and C-3 positions of the glucose unit of the amylopectin component. Although the

phosphorous content is low it is of great importance for the starch functionality and it will be clarified in section 2.3. (Bertoft, 2017)

In most common types of starch, the granule contains 20-30 % amylose and 70-80 % amylopectin, differing according to its source. The starch granule has crystalline and amorphous regions organized in onion-like layers. Amylopectin chains provide the crystallinity, while amylose is present in the amorphous structure.

Starch has many applications. For instance, it has been used in textiles as a sizing agent and as an adhesive in the paper industry. As aforementioned, due to the current growth of ecological consciousness, starch is also used in new applications such as disposable packages, cushioning and insulating materials, foam panels, building materials, wood adhesives, shoe components, among others. (Soykeabkaew, Thanomsilp, & Suwantong, 2015)

Starch-based foams have been developed as a replacement for polystyrene and studies have been carried out to overcome the brittleness and water sensitivity of starch itself. (Lawton, Shogren, & Tiefenbacher, 2004)

## **2.2 Starch foaming techniques**

The starch-based foams can be produced by many processes. Each foaming technique affects the final product properties like shape, cellular structure, density and mechanical properties. Thus, each production process suits a specific application. (Soykeabkaew et al., 2015)

Moisture is the driving force in most of the foaming techniques. Upon heating, exceeding the boiling point of water, the moisture turns into superheated steam, generating high pressure inside it. As the temperature increases, the starch granules gelatinize and fuse together. Due to the elevated pressure of the steam, bubbles are formed and expanded into a cellular structure. By the time that all of the moisture evaporates from the matrix and the heating is ceased, the foam cools down and reverts from a rubbery to a glassy state, creating the final solid foam structure. (Moraru & Kokini, 2003)

### **2.2.1 Microwave heating**

Microwaving is a fast and relatively inexpensive technique to add heat and is usually used for heating and/or cooking food. Popcorn is an example on how microwave energy can be applied for baking and expanding cereal foods. Microwave heating is therefore an interesting method for expanding starch into a foam, since it is a quick and “energy dense” process. One of the drawbacks of this technique is the difficulty to control some parameters during heating like temperature and water content. (Sjöqvist & Gatenholm, 2005)

Sjöqvist and Gatenholm (2005) prepared foams from different potato starches using free microwave heating with a frequency of 2450 MHz and 560 W for 3 minutes. Wide-angle X-Ray



scattering (WAXS) suggested that all of the granules had lost their original crystallinity, resulting in completely amorphous foams. The density of their native potato starch foams was 340 kg/m<sup>3</sup>. (Sjöqvist & Gatenholm, 2005)

The cellular structure of these foams is reported to be non-uniform, with open cells and thick cell walls. These are considered to be large, with sizes ranging between 100 µm and 1 mm.

Microwave heating is mostly used to produce starch foams from extruded pellets. The density of these foams was found to be higher than those produced by free microwave expansion, i.e. without previous extrusion process or by extrusion solely. The value obtained from this process were 217 kg/m<sup>3</sup> and a compressive modulus of 57 kPa. These are also more rigid, enabling them to absorb more energy (Jiang Zhou, Song, & Parker, 2007). The applications for this kind of foams are loose-fill packaging and heavy goods cushioning, due to the strength and stiffness provided by the thick cell walls.

### **2.2.2 Extrusion**

Starch extrusion has long been used in the food industry to produce expanded snacks. Through extrusion process it is possible to manufacture low-density foam materials. The most recent trend is to use starch as a component in manufacturing of extruded loose-fill packaging. (Pushpadass, Babu, Weber, & Hanna, 2008)

Extrusion of a starch and water mixture at temperatures above 100 °C leads to generation of voids, i.e., as the extrudate exits the die at high pressure conditions, the water steam expands forming the cellular structure. This process has three steps: nucleation, bubble growth and bubble stabilization. Foaming temperature, die diameter and screw speed are factors influencing cell size, cell distribution and foam density. (Willett, 2009)

The frequent extrusion processing conditions are a barrel temperature in the range of 120-170 °C and a screw speed between 70-400 rpm. Increasing of these two parameters usually increases the number of cells and therefore decreases the foam density.

Extrusion processing system produces large cell foams, resulting in low-density products. The densities reported for the extrusion process vary between 170 and 320 kg/m<sup>3</sup>, which are considered lightweight, depending, as mentioned above, on the processing conditions. These properties are very useful in applications where low weight is a priority, namely packaging for transportation. (Soykeabkaew et al., 2015)

### **2.2.3 Baking**

In applications where a complex shaped foam is required, for example disposable containers, the baking technique may be suited as the foam expands within a closed mold.

During baking, the starch granules gelatinize forming a thick paste. When the paste is heated, the entrapped water evaporates, expanding it. Then, once the paste fills up the mold, the remaining water evaporates and the foam finally solidifies and dries and with the final shape of the mold. Thus, the configuration of the foam is defined by the geometry of the mold. However, this technology is limited by the low drying rate of water removal from the paste, restricting the maximum wall thickness of the foam. (Shogren, Lawton, Doane, & Tiefenbacher, 1998; Soykeabkaew, Supaphol, & Rujiravanit, 2004)

To obtain well-shaped foams, processing parameters should be adequate. The most important of them, baking temperature and time, are usually in the range of 180-250 °C and 125-300 s, respectively, yet these are considered too long times and high energy consuming. (Soykeabkaew et al., 2015)

Baked foams often present a dense outer layer with small and closed cell structure, whereas the inside has large and open cells. The density of these foams is considered to be medium, varying between 0,1-0,3 g/cm<sup>3</sup>. (Mello & Mali, 2014)

Common uses for baked foams are mainly foam panels, disposal packages and containers, as mentioned earlier.

#### **2.2.4 Freeze-drying**

The freeze-drying process is also a foaming method used in production of starch-based foams. This technique consists of three steps: freezing, primary and secondary drying. When the temperature of an aqueous system is lowered, the water separates itself from the rest of the material, forming ice crystals. The solutes are then more concentrated and confined to the interstitial regions between the crystals. The final cellular morphology is formed as ice crystals sublimate during the primary drying step. Therefore, the pore structure is directly associated to the size and organization of the ice crystals formed during the freezing step. Finally, in the secondary drying step, the residual moisture evaporates. (Svagan, Samir, & Berglund, 2008)

The most important parameter to control is the freezing rate, which defines the number and organization of the crystals. Scanning Electron Microscopy (SEM) revealed that for lower temperatures, around -196 °C, the foam presented very small pores with an average cell size of 2,5 µm. This foam is considered to be a microporous foam. On the contrary, higher temperatures (-15 °C), give origin to a macroporous foam, with an average cell size of 430 µm. The density of these is similar to the one obtained by microwave heating with values ranging between 0,1-0,8 g/cm<sup>3</sup>. (Nakamatsu, Torres, Troncoso, Min-Lin, & Boccaccini, 2006)

These foams are useful whenever micro-scale and uniform cells are required. Some applications are for example scaffolds and tissue engineering. (Nakamatsu et al., 2006)

### **2.2.5 Supercritical fluid extrusion**

Supercritical fluid extrusion is a relatively novel technology for producing highly porous materials. This process uses supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) as a blowing agent instead of the typical steam. The main advantage is that the SC-CO<sub>2</sub> is an environmental friendly solvent and easily available.

The supercritical conditions of CO<sub>2</sub> are 31 °C and 7,38 MPa, which allow the extrusion to be held below 100 °C.

This technique can be divided in two stages: (i) flow of starch melts containing SC-CO<sub>2</sub> through the nozzle and (ii) exit of the extrudate from the die. As a result, the sudden pressure drop causes cell nucleation, followed by cell growth and expansion of the paste at the die exit as the pressure drops to the atmospheric level.

Many processing parameters can be controlled to define cell size, density and expansion such as pressure drop, proving that this process can be versatile. Thus, a wide range of foam structures with the desired mechanical properties can be achieved.

Supercritical fluid extrusion is successfully used to produce microcellular foams with cell size varying between 50-200 µm (Manoi & Rizvi, 2010).

## **2.3 Modification of starch-based foams**

Native starch foams have low water resistance and low flexibility. Due to the many free hydroxyl groups on glucose molecules, which can easily form hydrogen bonds with the surrounding moisture, starch is hydrophilic.

Furthermore, these foams suffer from a lack of strength and stiffness, being limited in use, especially for packaging for transportation of heavy goods (Guan, Fang, & Hanna, 2004).

The next sections summarize how starch-based foams can be modified in order to improve their performance.

### **2.3.1 Chemical modification**

A method for improving the water resistance of native starch is to turn its hydroxyl groups, which are hydrophilic, into acetyl groups, which are larger and significantly less polar. This change leads to an increase in its hydrophobicity and as a result a better resistance to moisture (Guan et al., 2004).

Water resistance can also be bettered with the addition of a crosslinking agent. This prevents interactions between the starch and water by establishing network structures within the starch material. It was proven that glyoxal could function as a crosslinking agent reducing the hydrophilicity of starch foams. (Nabar, Narayan, & Schindler, 2006)

### 2.3.2 Polymer blends

A great number of synthetic polymers have also been blended with starch to produce more flexible and water-resistant foams.

One way to overcome the water sensitivity is to blend starch with other hydrophobic polymers. Mixing with natural rubber or with chitosan has shown to improve evidently the moisture resistance in terms of water solubility and absorption. (Kaisangsri, Kerdchoechuen, & Laohakunjit, 2014)

In the work by Kaisangsri *et al.* (2012) a biodegradable foam tray from cassava starch blended with natural fiber and chitosan was developed. The results showed that for 30 % kraft fiber and 4 % chitosan solution, the foam had properties similar to polystyrene. The density achieved for this starch-based foam was 0,14 g/cm<sup>3</sup>. (Kaisangsri, Kerdchoechuen, & Laohakunjit, 2012)

The addition of latex increases the density of the foam, it also improves its flexibility. The properties of these foams are equivalent to the commercial ones and may be adjusted by changing the latex concentration (Shey, Imam, Glenn, & Orts, 2006).

An insoluble foam was developed by crosslinking starch with chitosan. The interactions between the amine groups of chitosan and the phosphate groups of starch allowed the foam to remain intact while in water (Deng & Catchmark, 2014)

In baked foams a variety of polymers has been blended with starch such as poly (vinyl acetate) (PVA), poly (lactic acid) (PLA), poly( $\epsilon$ -caprolactone) (PCL), latex and chitosan. It was shown an evident improvement in strength as well as in flexibility of the foams by adding these polymers. The mechanical properties, of the blend foams increased with the increase in polymer content, although rigidity was reduced. (Deng & Catchmark, 2014; Kaisangsri *et al.*, 2014; Shogren, Lawton, & Tiefenbacher, 2002; Soykeabkaew *et al.*, 2015)

In the study by Willett and Shogren (2002), in which the production process was twin-screw extrusion, the density of foams blended with PLA or poly (hydroxyester ether) (PHEE) was found to be decreased, since the polymer particles could act also as nucleating agent. The densities obtained in this study were in the same range as those of commercial starch loose-fill foams, having a density for potato starch foams with no resin of 40,6 kg/m<sup>3</sup>, decreasing for 25,2 kg/m<sup>3</sup> with 10 % PLA and 23.2 with 10 % PHEE (Willett & Shogren, 2002).

### 2.3.3 Fillers

Fillers are particulate materials, mostly inert, added to polymers with the aim of improving physical properties or to reduce the cost of the composite. Reinforcing fillers, particularly, are added to enhance some mechanical properties such as modulus, strength, stiffness, etc.. (Fried, 2000)

Natural fibers, for example, have been introduced in starch-based foams, showing that at a certain amount of fiber an improvement in mechanical properties was noticeable. One of the main reasons for using natural fibers as reinforcements is that both starch and cellulose are chemically similar, ensuring a good compatibility and interaction between them. (Monteiro, Martins, Magalhães, & Carvalho, 2016)

A great number of fibers have been studied to be used as fillers, like, soft wood, aspen, jute, flax, eucalypt, cellulose, kraft pulp and malt bagasse. (Soykeabkaew et al., 2004)

Soykeabkaew *et al.* incorporated jute and flax fibers in the starch-based paste and reported that both flexural strength and flexural modulus of elasticity was remarkably improved compared the non-reinforced foam. However, between both types of fiber, jute fibers appeared to be a better reinforcing agent compared to the other. In terms of density, for a fiber content of 1 % the average density of jute-reinforced starch-based foams was 0,223 g/cm<sup>3</sup> as for the flax-reinforced foam the density achieved was 0,248 g/cm<sup>3</sup>. (Soykeabkaew et al., 2004)

Other fillers tested were residues from agricultural crops. Starch-based foams reinforced with grape wastes, cardoon wastes and barley straw fibers showed an increase in rigidity, strength and also toughness. The biggest value of energy absorbed per unit achieved was 4,54 MJ/m<sup>3</sup> using with barley straw as filler. (Lopez-Gil, Silva-Bellucci, Velasco, Ardanuy, & Rodriguez-Perez, 2015)

Finally, talc was also employed to act as nucleating agent. A nucleating agent narrows the cell size distribution of the foams, by creating sites for the vaporization of water. This leads to the formation of foams with smaller cells and a small cell size distribution. However, the higher the content of talc, the higher the density of the foam. The best results were obtained for 1 % talc, yielding the maximum expansion ratio of the foam. (Jiang Zhou, Song, & Parker, 2006)

#### **2.3.4 Blowing agents**

Blowing agents, also known as foaming agents, are substances capable of producing gas and therefore generating cells in polymeric materials. They can be distinguished as physical or chemical blowing agents. Physical blowing agents act by a phase change while the chemical blowing agents produce gas by either thermal decomposition or chemical reaction with other components in the polymer mixture. (Heck & Peascoe, 2002)

As described before, water is commonly used as a physical foaming agent. As the boiling temperature of water is achieved, steam is generated creating the cells. Thus, cell growth depends on the amount of steam created.

Ethanol has also been employed as a blowing agent in extruded starch acetate blends, showing an increase in radial expansion of the foam. However, at too high content of ethanol, the cells

collapse. In this work the lowest bulk density achieved was 13,3 g/ml, which corresponded to a content of ethanol of 16 % for a PLA/starch blend. (Guan et al., 2004)

In the work by Zhou and Hanna (2004) secondary blowing agents such as pentane, ethyl acetate and sodium bicarbonate were used in a water foaming process. Pentane and ethyl acetate showed more effectiveness in increasing cell density. Sodium bicarbonate for instance reduced the cell density. The specific volume achieved for foams with sodium bicarbonate as secondary blowing agent ranged between 10 ml/g and 22 ml/g depending on the content of other additives. However it produced cells with very uniform sizes and increased the specific volume of the foam. (Jiahua Zhou & Hanna, 2004)

## 3 Materials and Methods

### 3.1 Raw materials

Native potato starch purchased from Diverembal was selected as the polymer matrix. Distilled water was employed as the blowing agent.

With the aim of improving the mechanical properties, wood fibers were used as reinforcement agents. Populus L. fibers, commonly used in medium density fiber panels, were provided from Valbopan-Fibras de Madeira S.A (Nazaré, Portugal).

Sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) was used as a secondary blowing agent and was supplied by PanReac AppliChem. To ensure the activity of  $\text{NaHCO}_3$ , which occurs at around a pH of 4, and also to prepare the chitosan solution, propionic acid was also chosen as a raw material. The acid was supplied by Fluka Chemika.

Finally, pure chitosan (molecular weight around 300 kDa, degree of deacetylation >85%) was selected as crosslinking agent and was supplied by Golden-Shell Pharmaceutical Co. Ltd (Zhejiang, China) in form of a powder and was prepared as follows.

#### 3.1.1 Chitosan preparation

Chitosan solution was prepared as described below:

- (i) 60 g of propionic acid were dissolved in 940 L of distilled water.
- (ii) 50 g of chitosan powder were added to 950 L of the previous solution and maintained under mechanical agitation until complete dissolution at 60 °C during 6 hours.

### 3.2 Production of the paste

To determine the amount of each raw material used in the paste Table 1 presents the base of calculus that was used.

**Table 1: Base formulation.**

Foam code	B_0.05	
Raw material	Compound:starch	%
Starch	-	47,6
Water	1:1	47,6
Chitosan	0.01:1	0,5
Fiber	0.04:1	1,9
NaHCO <sub>3</sub>	0.05:1	2,4

In order to produce the paste needed to form the foam, a rigorous experimental protocol was followed.

Firstly, water was mixed with the fiber. Since the dry fiber is hydrophobic, this should be wet before adding the other compounds avoiding that the fiber migrates to the surface of the foam at the end of the procedure.

Then, chitosan solution was added to ensure that the fiber is wet and to facilitate the addition of starch. The starch was then added. This mixture was blended for two minutes in a mechanical stirrer until a homogeneous paste was formed. The mechanical stirrer used was a Heidolph RZR 2041 at approximately 850 rpm.

Once the previous step was concluded, the paste had to be acidified so that the activity of the NaHCO<sub>3</sub> is enhanced. Propionic acid was used to acidify the paste. The pH was controlled with a Hanna Instruments 2211 pH/ORP Meter coupled with an HI1053B electrode with conical tip as shown in Figure 2, which is well suited for semi-solid samples, just like the starch-based paste.

**Figure 2: pH meter (left) and HI1053B electrode (right)**



Finally,  $\text{NaHCO}_3$  was added to the mixture with constant manual stirring until the mixture was homogenized. In this step is noticeable that the paste started to expand within the beaker.

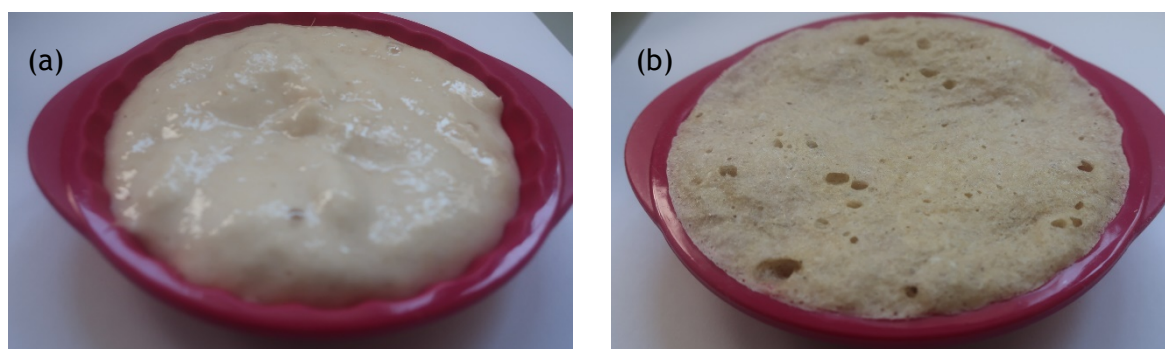
The final paste was then transferred to a silicone mold.

### 3.3 Microwave foaming

Microwave foaming process was performed in a conventional microwave oven model Kunft with a 2450 MHz frequency. Moreover, a silicone mold was used mainly because on the one hand the foams could be easily demolded and on the other hand silicone does not absorb much microwave radiation.

The mold with the paste was then placed at the center of the rotating plate and then heated at 950 W during 5-6 min. Finally, the foams remain inside the microwave oven to cool down for 3 minutes, avoiding their shrinkage during the final condensation of the entrapped water. Foaming time depends on the composition, particularly on the content of water. Thus, the specific foaming time for each formulation is detailed in Appendix 1. Excessive heating may lead to burning of the foams.

Figure 3 shows a picture of one of the foams produced before and after microwave heating.



**Figure 3:** Foam before (a) and after (b) microwave heating.

### 3.4 Physico-mechanical properties characterization

For the physico-mechanical characterization, the foams were cut into rectangular blocks with 50 mm width and length with a blade. The average height of the samples is 20 mm, thus the cross-sectional area of the foams varies around 2500 mm<sup>2</sup>. All the values presented in the results' section are an average of at least three determinations.

### 3.4.1 Determination of density

The apparent density of the foams was calculated by the ratio between their weight and volume as given by

$$d = \frac{W}{A \times h} \quad (3.1)$$

$W$  represents the weight of the sample,  $A$  the cross-sectional area and  $h$  the height. The density,  $d$ , is expressed in  $\text{kg/m}^3$  as determined by the normative NP EN 323. The samples width, length and height were measured with a digital caliper and their weight was measured in a precision balance.

### 3.4.2 Determination of moisture content

After being cut into the desired shape, the samples were weighed and put in the stove at a  $103^\circ\text{C}$  until a constant mass is achieved, according to the normative NP EN 322. A constant mass is considered when two successive weightings measured with at least 6 hours interval don't differ more than 0,1 %. After cooling the samples in a desiccator until room temperature the samples are newly weighed.

The moisture content,  $H$ , in weight percentage is then calculated by,

$$H = \frac{m_H - m_0}{m_0} \times 100 \quad (3.2)$$

where  $m_H$  is the initial mass of the sample in grams and  $m_0$  the mass of the sample in grams after drying.

### 3.4.3 Determination of the internal bond

The internal bond strength (IB) was measured according to the normative NP EN 319 in which the foam blocks are glued to the claws of the test machine with a hot melt glue. After the drying of the glue the foam-claw system is kept in a controlled humidity and temperature environment for 24 h. Figure 4 shows a picture of this system.



**Figure 4:** *Foam-claw system to determine internal bond.*

The sample is then tested at a constant rate until it breaks.

The results are expressed in N/mm<sup>2</sup> and determined through the following equation.

$$f_{t\perp} = \frac{F_{max}}{a \times b} \quad (3.3)$$

$F_{max}$  is the maximum force in N,  $a$  and  $b$  are the length and width of the sample, respectively and  $f_{t\perp}$  is the tensile strength perpendicular to the samples faces.

#### 3.4.4 Compressive tests

A Macmesin Multitest 1-d testing machine coupled with a 1000 N load cell was used to compress the samples as shown in Figure 5.



**Figure 5:** *Macmesin Multitest 1-d testing machine (left); Macmesin 1000 N load cell (right).*

A 4470 mm<sup>2</sup> rectangular plate was used to distribute the load on the sample. The strain rate which was defined as 1 mm/min was kept constant during the tests and the data was recorded by software Emperor™ Lite.

The compressive modulus of elasticity of samples was calculated based on the slope of the initial linear part of the load-displacement curves.

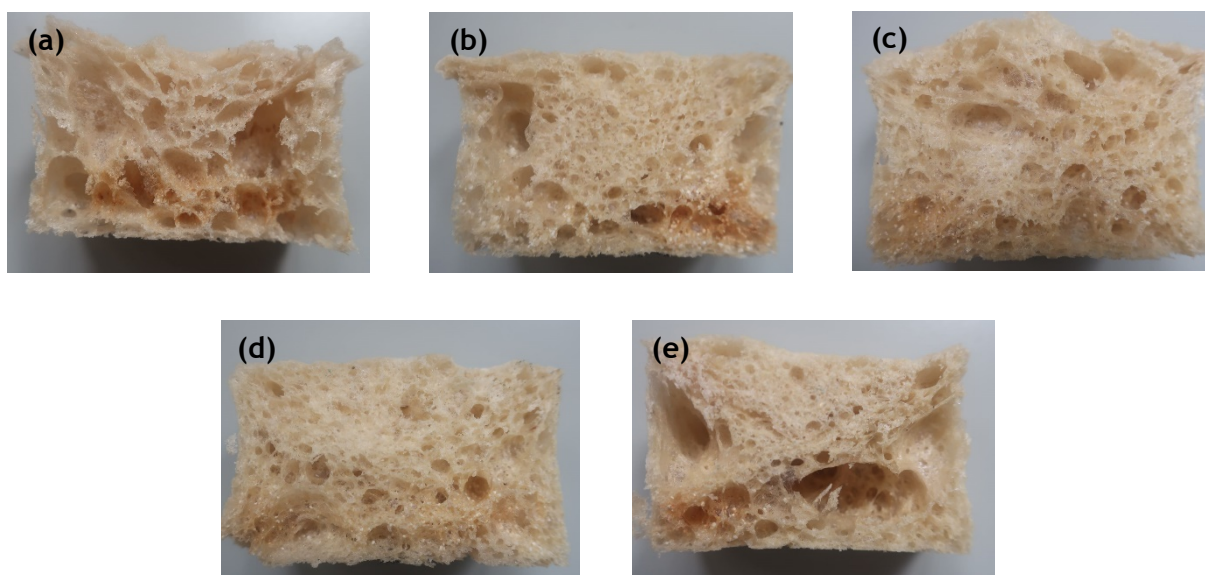
## 4 Results and discussion

### 4.1 Influence of the pH of the paste

The pH is a very important parameter when concerning a paste containing sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) as a chemical blowing agent, since it only reacts in the presence of acids. Although the formulation already has some acidic components, like chitosan solution and wood fiber, they are not acid enough to set off this chemical reaction. Thus, before studying the influence of  $\text{NaHCO}_3$  content, it was necessary to evaluate the influence of the paste's pH.

Propionic acid was used to acidify the paste, since this is also used to prepare the chitosan solution.

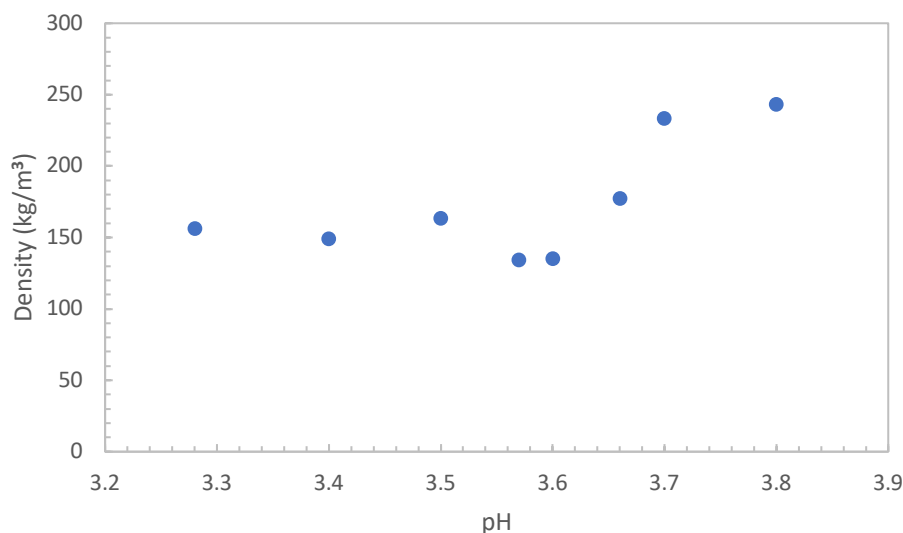
The pictures of a few foams during this analysis are shown in Figure 6.



**Figure 6:** *Influence of the pH on the foams. (a) pH=3,80; (b) pH=3,90; (c) pH=3,95; (d) pH=4,00; (e) pH=4,15.*

Although it may be difficult to visualize in the previous figure, for the same  $\text{NaHCO}_3$ :starch ratio (0,05), it was observed that the cell size decreases with the increase of the pH. Comparing Figure 6(a) and Figure 6(d) this difference is more evident.

In terms of produced foams' density, it was also clear that with the paste acidification the tendency is to decrease the density as depicted in the next figure. The results plotted in Figure 7 are only an estimate, since the values represent only one determination for each pH.



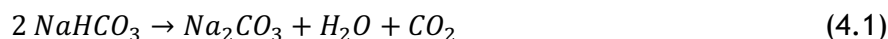
**Figure 7:** Influence of the paste pH on the density of the foams.

A major drawback on having a low pH is that, when adding  $\text{NaHCO}_3$  to the paste, it starts to expand immediately prior to microwave heating. This happened for every foam with a pH below 4. So, taking this phenomenon into consideration the pH of 4 was chosen as reference value for the coming sections.

## 4.2 Influence of sodium hydrogen carbonate content

In this work, different ratios of  $\text{NaHCO}_3$ :starch were studied in order to find a formulation that combines a low density and a high internal bond strength (IB) of the foams.

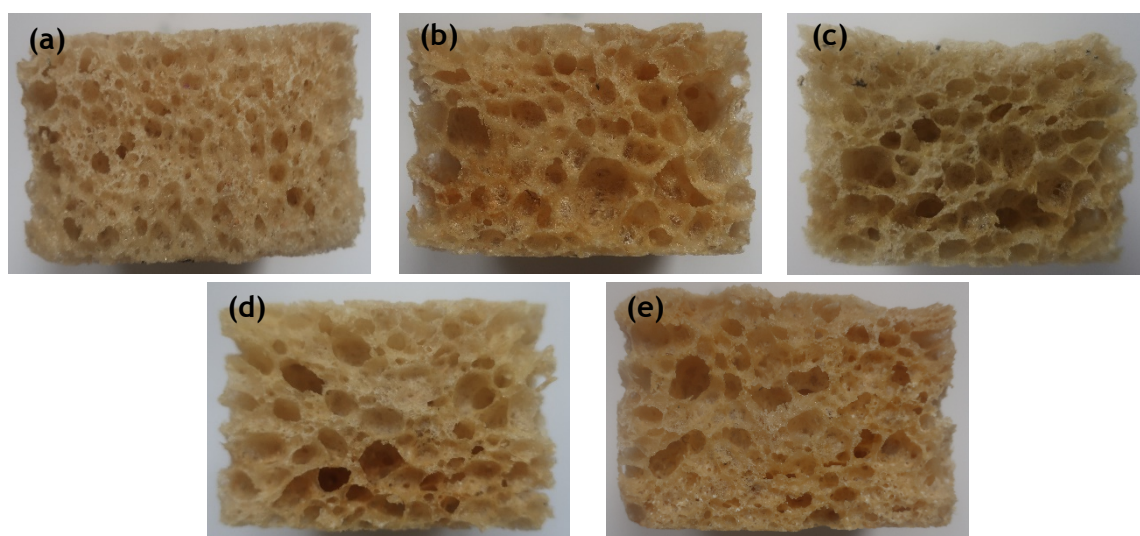
Sodium hydrogen carbonate, as previously explained, is used in the foam formulation as a secondary blowing agent. When  $\text{NaHCO}_3$  reacts with the acidic components of the batter, like fiber, chitosan and propionic acid, it releases carbon dioxide ( $\text{CO}_2$ ) according to equation 4.1,



causing the expansion of the paste and forming a cellular structure. Thus, increasing  $\text{NaHCO}_3$  content, it was expectable a higher foams expansion, due to an increased number of voids inside de foam and, as a consequence, a lower density.

The resulting foams show a narrow cell size distribution. With the increase of  $\text{NaHCO}_3$  the foams expand more and have larger cells as shown in Figure 8. The foams were given a code, relating the studied compound and its amount in the formulation, which for  $\text{NaHCO}_3$  the references are

B and the number is referring to the ratio  $\text{NaHCO}_3$ :starch and will be presented in Table 2. This logic is the same for the other studied compounds.



**Figure 8:** Foams after being cut: B\_0.01 (a), B\_0.03 (b), B\_0.05 (c), B\_0.07 (d), B\_0.09 (e).

Table 2 summarizes the formulation of each foam produced in this section.

**Table 2:** Foam codes and formulations for different  $\text{NaHCO}_3$  content.

Foam code	B_0.01	B_0.03	B_0.05	B_0.07	B_0.09
Raw material	Compound: starch	Compound: starch	Compound: starch	Compound: starch	Compound: starch
Starch	-	-	-	-	-
Water	1:1	1:1	1:1	1:1	1:1
Chitosan	0,01:1	0,01:1	0,01:1	0,01:1	0,01:1
Fiber	0,04:1	0,04:1	0,04:1	0,04:1	0,04:1
$\text{NaHCO}_3$	0,01:1	0,03:1	0,05:1	0,07:1	0,09:1

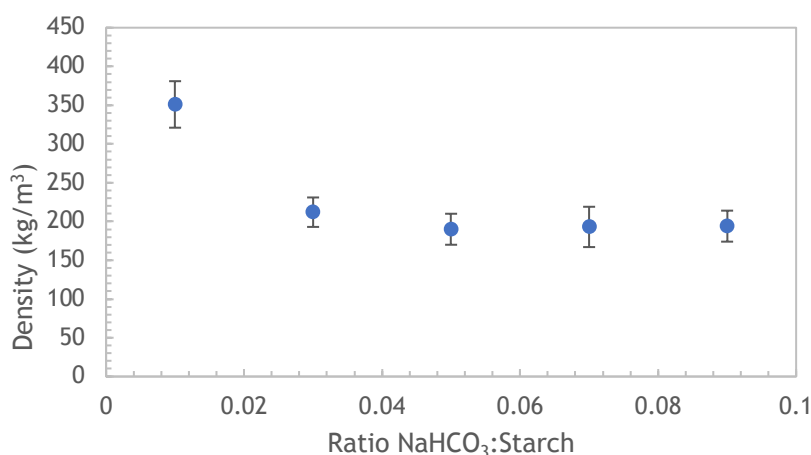


A foam with no  $\text{NaHCO}_3$  was also produced, even though due to its irregular shape it was impossible to determine its properties. This foam showed a big hole inside, which resulted from the coalescence of the gas bubbles. In fact, as explained before, the presence of the  $\text{NaHCO}_3$  helps to stabilize the gas bubbles during foam formation. A picture of this foam is shown in Figure 9.



**Figure 9:** Foam with no  $\text{NaHCO}_3$ .

The dependence of the densities of foamed blocks made from the previous formulations on the  $\text{NaHCO}_3$  content is shown in Figure 9.



**Figure 10:** Dependence of the density on the  $\text{NaHCO}_3$  content.

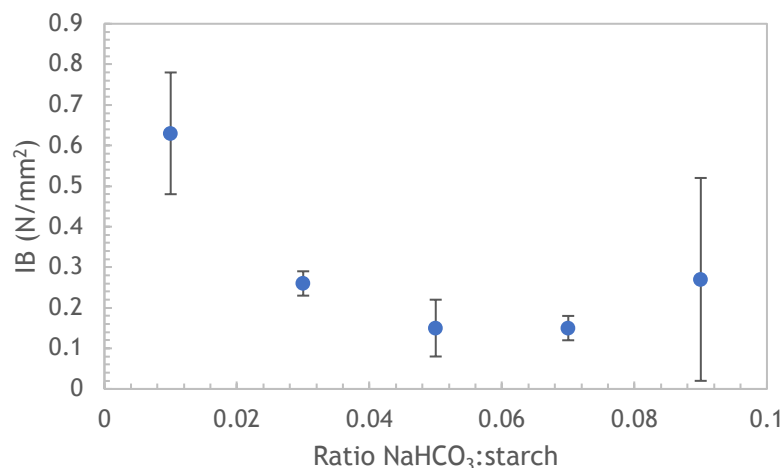
The data suggest that with increasing content of  $\text{NaHCO}_3$  for all formulations the density initially tends to decrease until reaching a plateau.

The minimum value of the density obtained was  $190 \text{ kg/m}^3$  corresponding to the foam with a ratio  $\text{NaHCO}_3$ : starch of 0,05. The resulting values are in agreement to those expected: the higher the content in  $\text{NaHCO}_3$ , the lower the density, reaching the plateau after 0,05 ratio  $\text{NaHCO}_3$ :starch.

The densities obtained fulfill the objective of having a lightweight foam, as the values do not exceed  $600 \text{ kg/m}^3$ .



The internal bond strength (IB) provides an overall evaluation of the foam's mechanical integrity, indicating how well the material is bonded together. The IB results of the foams versus their content on  $\text{NaHCO}_3$  are given in Figure 11.



**Figure 11:** *Dependence of the internal bond on the  $\text{NaHCO}_3$  content.*

Similarly, to what happens with the density of the foams, with the increasing of  $\text{NaHCO}_3$  content, the IB decreases. The cell size of the produced foams is smaller in foams with higher density, being close together and implying a higher value of IB.

Combining the two factors, it is desirable that the foam has lower densities and higher IB values. Thus, excluding the foam with 0,09  $\text{NaHCO}_3$ :starch ratio, which shows a large variability, the foams with the improved properties were the ones with the reference B\_0.03 followed by B\_0.05. However the chosen foam was B\_0.05 because visually it was the one with the most uniform cell size distribution.

In Table 3 are presented the values obtained for water content of each foam introduced in this section.

**Table 3:** *Variation of moisture content for variable NaHCO<sub>3</sub>:starch ratio.*

Foam Code	Ratio NaHCO <sub>3</sub> :Starch	Water Content (%)
B_0.01	0,01	14,6
B_0.03	0,03	15,1
B_0.05	0,05	12,3
B_0.07	0,07	12,1
B_0.09	0,09	17,8

B\_0.09 foams showed higher water content, probably due to a lower stabilization time.

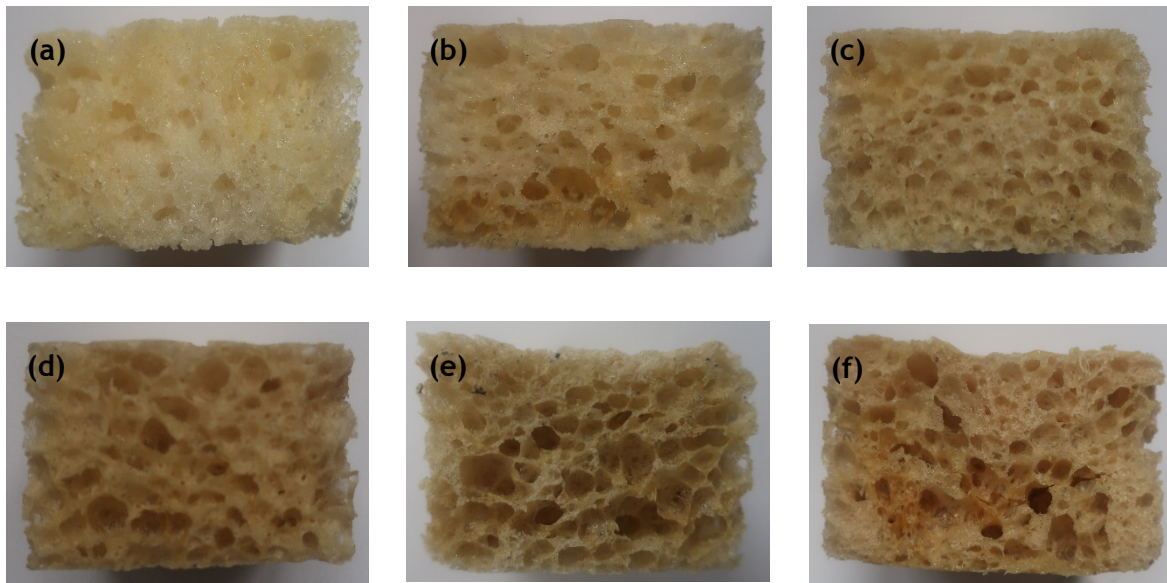
Evaluating each property and its corresponding results, the foam combining one of the lowest density with a high IB and also the foam which showed the most regular cellular structure was the one with the ratio of NaHCO<sub>3</sub>:starch of 0,05. For all the reasons mentioned above, this formulation was chosen as the optimum for NaHCO<sub>3</sub> content and will be used as reference for the upcoming sections.

### 4.3 Influence of fiber content

The fiber content was also studied, starting from the optimal formulation found in the previous section, in which the ratio fiber:starch was 0,04.

Wood fiber was added to the composites formulation in order to improve the mechanical properties of the foams. The wood fiber which is compatible with the starch matrix, reinforces as well as strengthens the foams, as predicted in literature (Monteiro et al., 2016).

Figure 12 depicts the resulting foams for each formulation of this section and are distributed in order of ascending fiber content, being Figure 12 (a) the foam with no fiber and Figure 12 (f) the foam with the highest amount of fiber.



**Figure 12:** *Foams after being cut: F\_0.00 (a), F\_200 (b), F\_100 (c), F\_300 (d), B\_0.05 (e), F\_400 (f).*

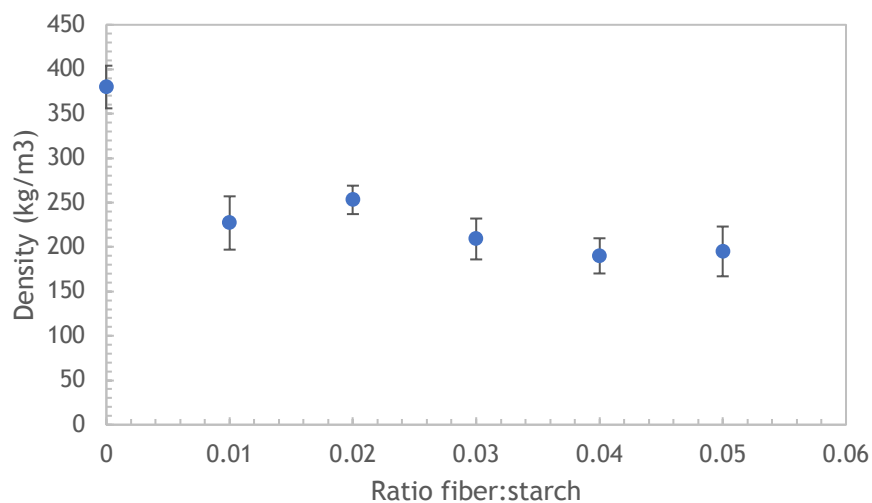
Regarding the previous figure, it is noticeable that with increasing content of fiber the cell walls become less brittle. This has to do with the reinforcing function of the fiber, resulting in a foam with tougher cells and consequently tougher foams.

The fiber: starch ratio was increased from 0 to 0,05. Above 0,05 it became impossible to blend the paste properly. All the formulations used to produce the foams depicted above are described in Table 4.

**Table 4:** Foam codes and formulations for different fiber content.

Foam code	F_0.01	F_0.02	F_0.03	B_0.05	F_0.05
Raw material	Compound: starch	Compound: starch	Compound: starch	Compound: starch	Compound: starch
Starch	-	-	-	-	-
Water	1:1	1:1	1:1	1:1	1:1
Chitosan	0,01:1	0,01:1	0,01:1	0,01:1	0,01:1
Fiber	0,01:1	0,02:1	0,03:1	0,04:1	0,05:1
NaHCO <sub>3</sub>	0,05:1	0,05:1	0,05:1	0,05:1	0,05:1

The results plotted in Figure 13 present the dependence of the foam densities on fiber content.

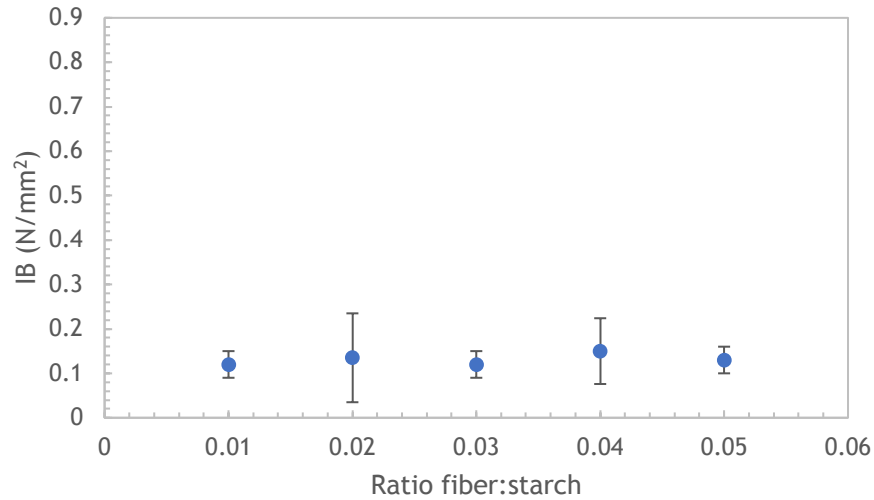
**Figure 13:** Dependence of the density on the fiber content.

The resulting data show that with increasing ratio of fiber:starch the density decreases to reach a plateau. Except for the foam F\_0.00 the densities range between 190 and 253 kg/m<sup>3</sup>, proving that the variation of fiber:starch ratio wasn't significant enough to cause big changes in the densities of the produced foams. Still, the lowest density was 190 kg/m<sup>3</sup> corresponding to the foam B\_0.05, which has a ratio fiber:starch of 0,04.

Comparing these results to the ones available in literature, Soykeabkaew *et al.* (2004) produced foams with similar densities using a baking process. Foams with jute and flax fibers were

produced with a content of 1 % fiber, having an average density of 223 kg/m<sup>3</sup> and 248 kg/m<sup>3</sup>, respectively.

Concerning the IB, the results are presented in Figure 14.



**Figure 14:** *Dependence of the internal bond on the fiber content.*

The resulting values were also identical between foams, thus practically inconclusive. This outcome points out the fact that the variation of fiber content was insufficient to make a difference in the foams' IB. Even though taking the cell structure into consideration, it was possible to see the effect of the fiber addition on the thickness of the cell walls, the results do not provide quantitative indication of actual mechanical reinforcement.

Table 5 presents the values obtained for the equilibrium moisture content of the present foams.

**Table 5:** *Variation of moisture content for variable fiber:starch ratio.*

Foam Code	Ratio Fiber:Starch	Moisture Content (%)
F_0.00	0,00	12,9
F_0.01	0,01	10,9
F_0.02	0,02	12,2
F_0.03	0,03	14,1
B_0.05	0,04	12,3
F_0.05	0,05	14,1

In terms of water content, the foam which showed the lowest percentage was F\_0.01, however the difference between foams was only 2-4 % evidencing that these reached the equilibrium value of water content.

In order to proceed the optimization, the formulation chosen was once again B\_0.05, which was the formulation that suggested the best combination of density and IB. The foam B\_0.05 had the lowest value of density ( $190 \text{ kg/m}^3$ ) and the highest value of IB, which was  $0,15 \text{ N/mm}^2$ .

This formulation will be carried forward to the next section, where the content of chitosan will be analyzed.

#### 4.4 Influence of chitosan content

In the present section, the effect of the chitosan content will be evaluated having formulation B\_0.05 as a starting point. This formulation has a ratio of chitosan:starch of 0,01.

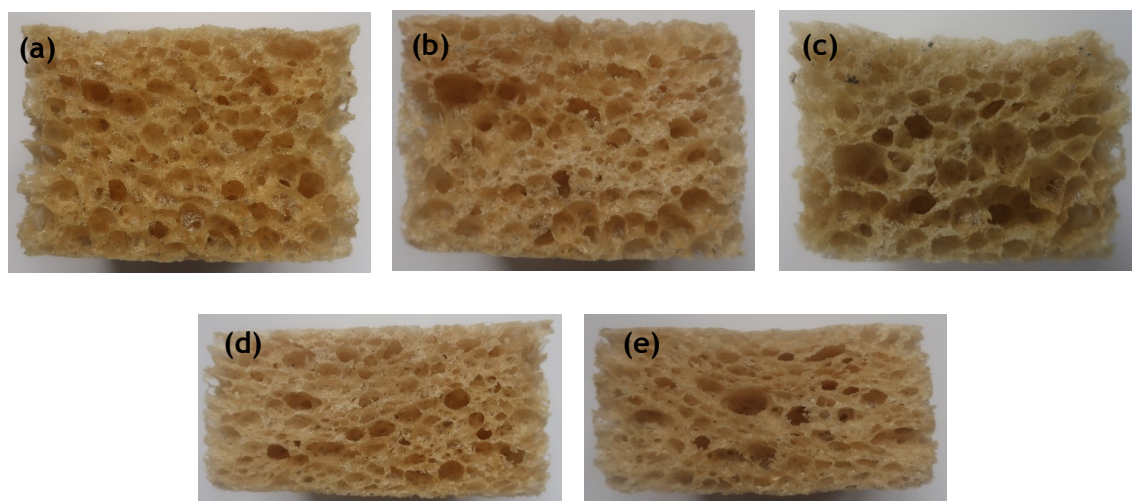
Based on the evidence presented in the section 2.3 (Modification of starch-based foams), chitosan was added to the starch-based foam's formulation in order to improve the foams properties, particularly to provide mechanical strengthening.

The ratio chitosan:starch was raised from 0 to 0,02. From 0,02 forward, the paste became thicker, making it hard to blend homogeneously. On the other hand, with no chitosan the fiber present in the formulation tended to agglomerate and to form small lumps of fiber. As a consequence the foam with no chitosan showed very irregular cell structure and surfaces, making it hard to measure density and IB, as seen in Figure 15.



**Figure 15:** *Foam with no chitosan.*

Figure 16 shows close-up images of all foams produced in this section which are placed in ascending order of chitosan content.



**Figure 16:** *Foams after being cut: C\_0.005 (a), C\_0.007 (b), B\_0.05 (c), C\_0.015 (d), C\_0.02 (e).*

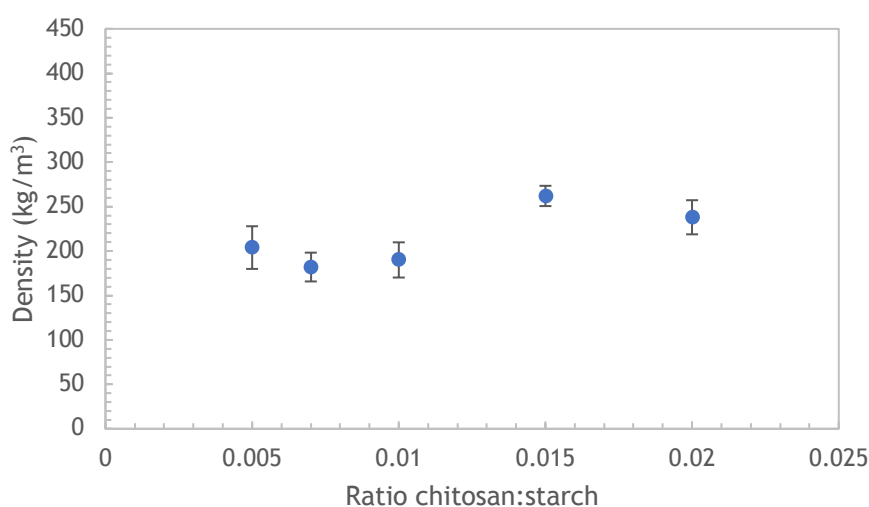
In terms of appearance, the foams from Figure 16 (a) to Figure 16 (c) show an increasing size of cells, maintaining in each foam the cell size uniform. In Figure 16 (d) and Figure 16 (e), it can be seen that the foams didn't expand as much as the others and the cell size is smaller and the cell size distribution is wider.

The corresponding formulations are summarized in Table 6.

**Table 6:** Foam codes and formulations for different chitosan content.

Foam Code	C_0.005	C_0.007	B_0.05	C_0.015	C_0.02
Raw material	Compound: starch	Compound: starch	Compound: starch	Compound: starch	Compound: starch
Starch	-	-	-	-	-
Water	1:1	1:1	1:1	1:1	1:1
Chitosan	0,005:1	0,007:1	0,01:1	0,015:1	0,02:1
Fiber	0,04:1	0,04:1	0,04:1	0,04:1	0,04:1
NaHCO <sub>3</sub>	0,05:1	0,05:1	0,05:1	0,05:1	0,05:1

The resulting values of density as a function of the ratio chitosan:starch are displayed in Figure 17.

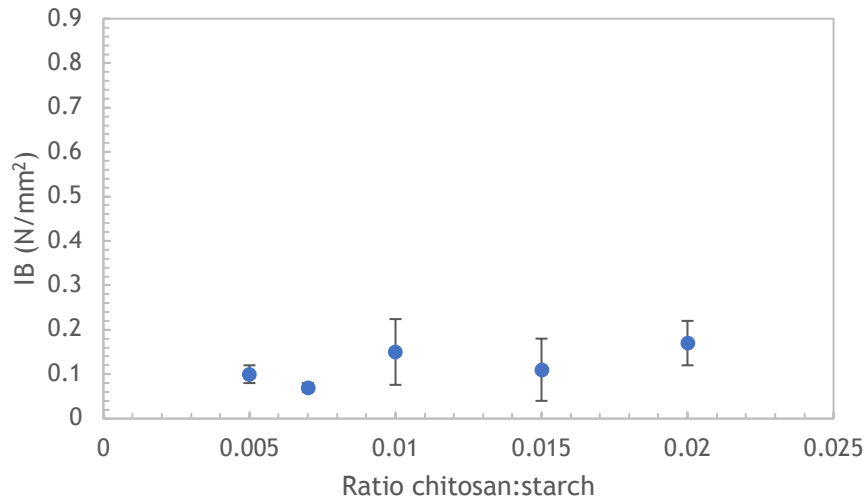
**Figure 17:** Dependence of the density on the chitosan content.

Assessing the graph presented on the previous figure, the minimum value of density obtained was 182 kg/m<sup>3</sup>, which is also the lowest achieved so far in this work. This density corresponds to the foam with a chitosan:starch ratio of 0,007. The highest value, not totally in agreement to what was expected, was achieved by the foam with a ratio of 0,015. The difference between the densities achieved for C\_0.015 and C\_0.02 were not very significant, as for the foam C\_0.02 it was already hard to blend the paste correctly to ensure an homogeneous mixture. Hence it



would be expected an increase of density, with the increase in chitosan content which was partially verified.

The IB values of the foams produced in this section are given in Figure 18.



**Figure 18:** *Dependence of the internal bond on the chitosan content.*

It was predicted that the IB would increase with the increase on chitosan content, as chitosan's function was to strengthen the foam, which implies a higher IB. In fact, the foam with the biggest amount of chitosan in the formulation (C\_0.02) is at the same time the foam with the highest IB. However, the other formulations didn't behave the same way.

In fact, the IB results in this section, were not particularly conclusive, since the values obtained are very similar. However, as mentioned before, adding more chitosan to the formulation made mixing the paste difficult and therefore the content was not increased further. Thus the variation of the ratio chitosan:starch didn't make a big difference on the achieved results. The large variability may have to do with the hardly uniform surface of the foams, as seen in Figure 16. Although the surfaces seem straight and the irregularities may appear to be insignificant, this has much influence on the IB results. The claws of the testing machine are not entirely parallel and glued to the foam, translating into lower reproducibility.

Nevertheless, combining both density and IB results, the foam which aggregates a low density and high value of IB is B\_0.05. C\_0.02 had the highest IB, but also had a high density and on the contrary C\_0.007 had the lowest density but also the lowest IB, being therefore B\_0.05 the foam with the best combined outcome.

The equilibrium moisture content of the foams is presented on Table 7.

**Table 7:** *Variation of moisture content for variable chitosan:starch ratio.*

Foam Code	Ratio Chitosan:Starch	Moisture Content (%)
C_0.005	0,05	16,5
C_0.007	0,007	20,4
B_0.05	0,01	12,3
C_0.015	0,015	16,0
C_0.02	0,02	16,0

There were small differences on the equilibrium moisture content, which was in the range of 12,3 % to 20,4 %. These results may have to do with the stabilization time of the foams, which may have been different for each formulation.

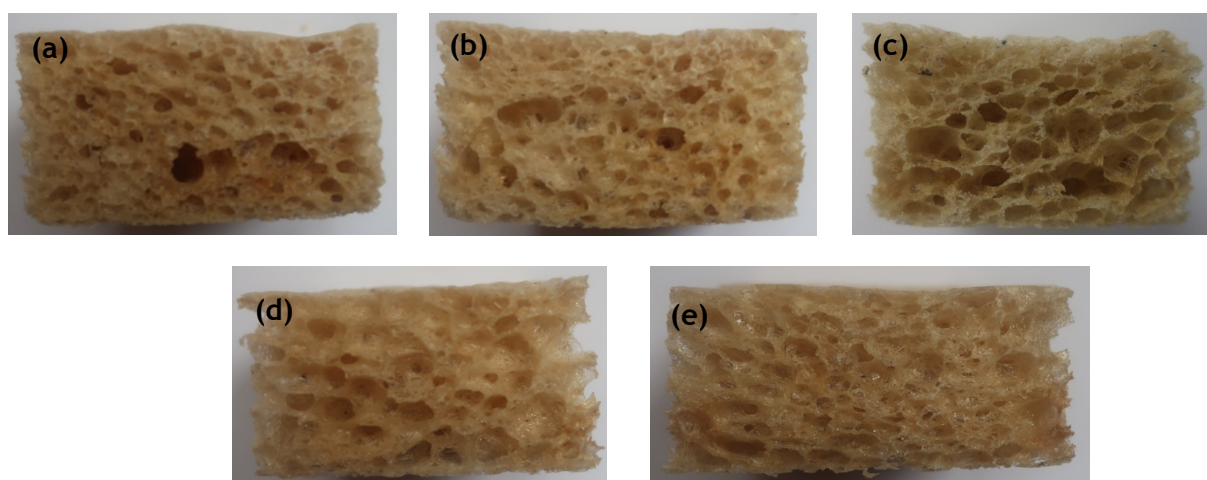
To conclude this section, the foam chosen to proceed to the next section was again B\_0.05. This foam presented the best combined properties.

## 4.5 Influence of water content

Another important parameter of the foam's formulation is the content of water. Having B\_0.05 as reference, in which the ratio water:starch was 1, foams with other ratios were produced as to evaluate the influence of water and to determine its optimal content.

Water is employed in the formulation as a physical blowing agent. According to literature presented on section 2.3, once heat is added, the boiling temperature of water is reached, generating steam and thus forming cells. Hence, the amount of steam created, which fully depends on the amount of water added to the mixture, determines the cell growth. So the higher the content of water, the larger the cells. (Moraru & Kokini, 2003)

The ratio of water:starch was increased from 0,9 to 1,5. Below 0,9 the mixture hadn't enough moisture to ensure an homogeneous blend. All formulations produced in this section are depicted in Figure 19 being Figure 19 (a) the foam with less water and Figure 19 (e) the foam with the higher amount of water in its formulation.



**Figure 19:** Foams after being cut: W\_0.95 (a), W\_0.90 (b), B\_0.05 (c), W\_1.25 (d), W\_1.5 (e).

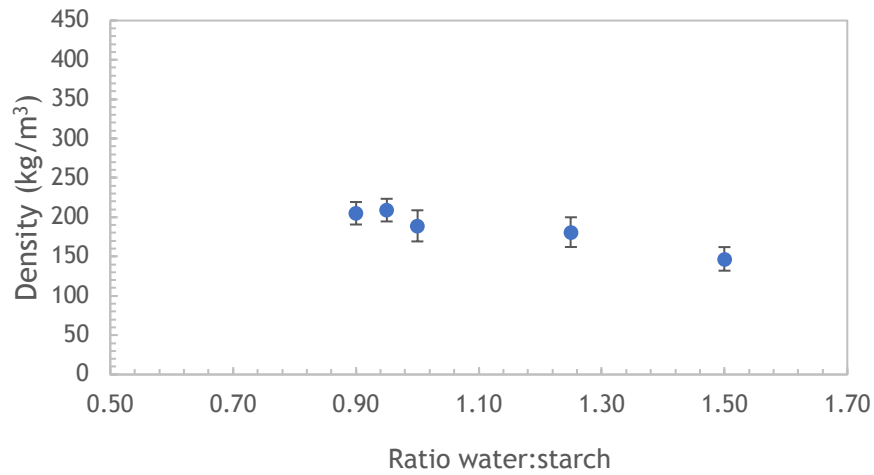
Visually the foams confirm the theory, that with increasing water content the cells also enlarge, having a greater expansion.

The formulations are described in Table 8.

**Table 8:** Foam codes and formulations for different water contents.

Foam code	W_0.90	W_0.95	B_0.05	W_1.25	W_1.50
Raw material	Compound: starch	Compound: starch	Compound: starch	Compound: starch	Compound: starch
Starch	-	-	-	-	-
Water	0,9:1	0,95:1	1:1	1,25:1	1,5:1
Chitosan	0,01:1	0,01:1	0,01:1	0,01:1	0,01:1
Fiber	0,04:1	0,04:1	0,04:1	0,04:1	0,04:1
NaHCO <sub>3</sub>	0,05:1	0,05:1	0,05:1	0,05:1	0,05:1

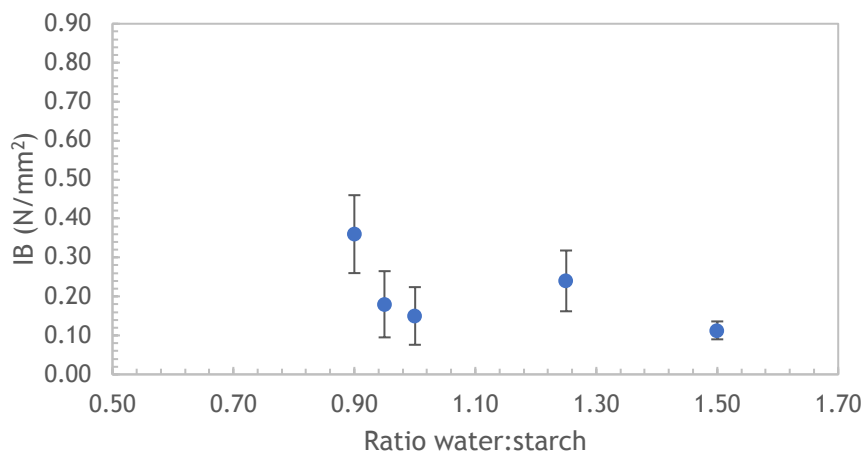
The dependence of the densities of the foams on the ratio water:starch is plotted in Figure 20.



**Figure 20:** *Dependence of the density on the water content.*

The results on the influence of water on the density turned out as expected: with the increase in amount of water the density decreases. So the minimum density achieved was 147 kg/m<sup>3</sup> corresponding to W\_1.50 and the highest 209 kg/m<sup>3</sup> which is relative to the foam with the higher ratio water:starch (0,95).

Concerning the IB, the graph in Figure 21 presents the obtained IB values as a function of the ratio water:starch.



**Figure 21:** *Dependence of the IB on the water content.*

Analyzing the previous figure, the resulting values for the IB determination of these foams are in agreement with the values obtained for density as with the increase of water, the IB tends to decrease. The highest value was achieved by W\_0.90, which also is very dense. The minimum value (0,11 N/mm<sup>2</sup>) corresponds to the foam with the lowest density, which makes sense as with the increase of cell size, resulting in low density, the cell walls become more fragile producing foams with lower IB's.

Therefore, combining both results, the foam W\_1.25 suggests the better result, having a relatively low density and one of the highest IB.

Table 9 presents the equilibrium moisture content of foams with variable water:starch ratio.

**Table 9:** *Variation of moisture content for variable water:starch ratio.*

Foam Code	Ratio Water:Starch	Moisture Content (%)
W_0.90	0,90	14,9
W_0.95	0,95	12,7
B_0.05	1	12,3
W_1.25	1,25	18,0
W_1.50	1,50	18,7

With the raise of the water content it is coherent that the moisture content also increases, which is verified except for W\_0.90. In fact it is likely that the stabilization time of this foam was insufficient hence this behavior.

## 4.6 Optimal formulation

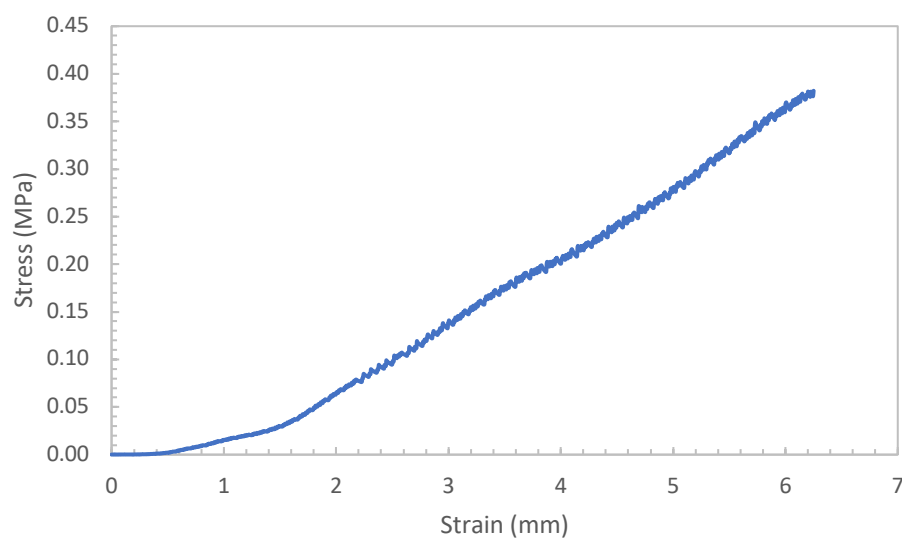
Finally, having studied the influence of every raw material used, it was possible to choose the foam, which showed the most improved properties. The main properties evaluated were density and IB, but the moisture content was also taken into account.

Thus, Table 10 presents a summary of the proportion of raw materials and properties of the foam chosen.

**Table 10:** *Summary of the properties of the optimized foam.*

<b>Foam Code</b>	<b>W_1.25</b>
<b>Raw Materials</b>	<b>Compound:starch</b>
<b>Starch</b>	-
<b>Water</b>	1,25:1
<b>Chitosan</b>	0,01:1
<b>Fiber</b>	0,04:1
<b>NaHCO<sub>3</sub></b>	0,05:1
<b>Mechanical properties</b>	
<b>Density (kg/m<sup>3</sup>)</b>	181
<b>IB (N/mm<sup>2</sup>)</b>	0,24
<b>Moisture content (%)</b>	18

To conclude this section, compression modulus of elasticity was also measured, as to compare the starch-based composite foams with other commercially used foams. The compression modulus was calculated as described in section 3.3.4 (Compressive tests) and is the slope of the linear part of the stress and strain curve, as depicted in Figure 22.

**Figure 22:** *Stress and strain curve for W\_1.25 foams.*

The resulting compressive modulus of elasticity for W\_1.25 foams was 0,086 MPa. The main difficulty of this test has to do with the cellular structure of the foam, since because of it the foams start to break not all the same time, crushing the cells.

It is hard to compare all these results with the ones presented in the literature, because different processing methods and different combinations of raw materials result in distinct mechanical properties. For instance, free microwave foaming was only used by Sjöqvist and Gatenholm, but the composition and preparation of the paste was different.

Nevertheless, the obtained results for W\_1.25 foam were compared to values found on literature for rigid polyurethane (PU) foams and also for a commercial extruded polystyrene foam and these values are summarized in Table 11. (Thompson, McCarthy, Lidgren, & Ryd, 2003)

**Table 11:** *Comparison between produced foam and rigid polyurethane foams.*

<b>Material</b>	<b>Starch-based foam (W_1.25)</b>	<b>Rigid polyurethane foams (Thompson et al., 2003)</b>		<b>Rigid polystyrene foam (RoofMate)<sup>1</sup></b>
Density (kg/m <sup>3</sup> )	181	158	209	33
Compressive modulus (MPa)	0,086	38,7	79,3	12

In fact, the foam produced in this work has a much lower compressive modulus than of rigid PU foams.

Comparing both the starch-based foam and a commercial extruded polystyrene foam, it is not likely that the first has a compressive modulus so low, because it is possible to have a sense of both foams' rigidity only by touch, and the starch-based foam seems much more rigid than the polystyrene one. Thus, it is presumable that the compression test wasn't able to measure the true compressive modulus of the foam. Because the foam structure is brittle, the compression causes successive crushing of the cell walls. That explains the "stepladder" shape of the stress-strain curve that is visible upon close inspection. The true compressive modulus would only be measurable for very low displacements, which is not possible with the current equipment.

<sup>1</sup> Data extracted from a technical datasheet for a ROOFMATE™ polystyrene foam from Dow Chemical.

## 5 Conclusions

Microwave heating is a fast and inexpensive technique to expand the starch-based paste, making possible the production of a foam within a few minutes.

The addition of different additives with specific functions should let the properties of the foam be tailored for a specific application. Thus, one of the main objectives of this work was to find a formulation which combined a low density and a high internal bond in order to produce a material suitable for the furniture industry.

For instance, using  $\text{NaHCO}_3$  as a chemical blowing agent increased cell size and as a consequence decreased the density of the foam. Also, the pH of the initial paste was an important parameter studied, since it affects the gas releasing reaction of  $\text{NaHCO}_3$ . The optimum ratio of  $\text{NaHCO}_3$ :starch combined with a pH of 4 was 0,05.

Furthermore, the variation of the fiber content wasn't enough to show a significative difference on the IB values, which ranged between  $12 \text{ N/mm}^2$  and  $15 \text{ N/mm}^2$ .

Chitosan was employed as a crosslinking agent, particularly because of the interaction between its amine groups and the phosphate groups of starch. The introduction of this raw material in the starch-based paste strengthened the foam mechanically resulting in an increase of the internal bond strength, however the results were very similar, not enabling an accurate interpretation of the data. The maximum value was obtained by B\_0.05 and was  $0,15 \text{ N/mm}^2$ .

Finally, water was used as a physical foaming agent, because with the increase of the amount of water, the steam created by the addition of heat generates voids and as a consequence a cellular structure. So, it was expected that the higher the amount of water the lower the density. The best result of this section was therefore W\_1.25 which had a density of  $181 \text{ kg/m}^3$  and a IB of  $0,24 \text{ N/mm}^2$ . This foam was then chosen as the optimal formulation of this research.

In terms of the compressive modulus of the chosen foam, it wasn't possible to obtain a reliable result, as the foam cells were being crushed during the test due to its brittleness.

Nevertheless, the proposed objectives for this work were successfully accomplished. A lightweight foam was produced by microwave heating with a paste as starting point, comprising a low density with a relatively high internal bond strength.



## 5.1 Limitations and Future Work

The main limitation of this work was the difficulty to find values of reference for the parameters studied in order to have a benchmark to compare with.

Furthermore, contrary to what may look like, the foams aren't completely straight, because the mold is open and the expansion is free. This issue hinders both the internal bond determination, because the claws cannot be glued to 100 % of the surface of the foam and also the compressive tests.

In the future, there are some points that could be explored as the case of adding glycerol as plasticizing agent to soften the foam and give the foam a little more elasticity, not allowing the foam cells to fracture during the compression. Also, to produce a foam within a closed mold may bring some improvement in terms of smoothness of upper surface of the foams, which will certainly improve the deviations of the IB results and compressive tests.

Finally, it would be profitable to use an acid, to adjust the pH, which only acts during heating, as it is the case of the sodium acid pyrophosphate. This prevents the growth of the paste prior to heating, ensuring a more controlled expansion.

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# Appendix 1

Table 12: Detailed formulations and foaming times.

Foam reference	B_0.01		B_0.03		B_0.05		B_0.07		B_0.09	
Raw material	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%
Starch	-	48,5	-	48,1	-	47,6	-	47,2	-	46,7
Water	1:1	48,5	1:1	48,1	1:1	47,6	1:1	47,2	1:1	46,7
Chitosan	0,01:1	0,5	0,01:1	0,5	0,01:1	0,5	0,01:1	0,5	0,01:1	0,5
Fiber	0,04:1	1,9	0,04:1	1,9	0,04:1	1,9	0,04:1	1,9	0,04:1	1,9
NaHCO <sub>3</sub>	0,01:1	0,5	0,03:1	1,4	0,05:1	2,4	0,07:1	3,3	0,09:1	4,2
Heating time (min'sec'')	5'45''		5'20''		5'15''		5'10''		5'00''	
Foam reference	F_0.01		F_0.02		F_0.03		F_0.05			
Raw material	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%		
Starch	-	48,3	-	48,1	-	47,9	-	47,4		
Water	1:1	48,3	1:1	48,1	1:1	47,9	1:1	47,4		
Chitosan	0,01:1	0,5	0,01:1	0,5	0,01:1	0,5	0,01:1	0,5		
Fiber	0,01:1	0,5	0,02:1	1,0	0,03:1	1,4	0,05:1	2,4		
NaHCO <sub>3</sub>	0,05:1	2,4	0,05:1	2,4	0,05:1	2,4	0,05:1	2,4		
Heating time (min'sec'')	5'20''		5'15''		5'15''		5'10''			
Foam reference	C_0.005		C_0.007		C_0.015		C_0.02			
Raw material	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%		
Starch	-	47,7	-	47,7	-	47,5	-	47,4		
Water	1:1	47,7	1:1	47,7	1:1	47,5	1:1	47,4		
Chitosan	0,005:1	0,2	0,007:1	0,3	0,015:1	0,7	0,02:1	1,0		
Fiber	0,04:1	1,9	0,04:1	1,9	0,04:1	1,9	0,04:1	1,9		
NaHCO <sub>3</sub>	0,05:1	2,4	0,05:1	2,4	0,05:1	2,4	0,05:1	2,4		
Heating time (min'sec'')	5'40''		5'30''		5'30''		5'40''			
Foam reference	W_0.90		W_0.95		W_1.25		W_1.50			
Raw material	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%	Compoundstarch	%		
Starch	-	50,0	-	48,8	-	42,6	-	38,5		
Water	0,9:1	45,0	0,95:1	46,3	1,25:1	53,2	1,5:1	57,7		
Chitosan	0,01:1	0,5	0,01:1	0,5	0,01:1	0,4	0,01:1	0,4		
Fiber	0,04:1	2,0	0,04:1	2,0	0,04:1	1,7	0,04:1	1,5		
NaHCO <sub>3</sub>	0,05:1	2,5	0,05:1	2,4	0,05:1	2,1	0,05:1	1,9		
Heating time (min'sec'')	5'45''		5'50''		6'00''		6'10''			

